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EXECUTIVE SUMMARY

DISTILLATION OF LIQUID WASTE FROM THE FREON-BASED DRY CLEANING PROCESS

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The BNPD-Services Central Maintenance Facility laundry has six Freon-based dry cleaning machines. The waste from these machines contains low levels of activity and Freon 113 in amounts varying from 1 - 90 % by weight. Solidification of this waste is less desirable than incineration because the waste volume is subsequently increased. Incineration of the waste, however, was not recommended unless the Freon content could be reduced to the point where corrosion of incinerator components by resulting acid gases was not a concern. Work in this report deals with the removal of Freon 113 from the waste by simple distillation.

The Freon content of the waste can be effectively reduced to less than 4% by distillation in the temperature range 60-85°C. Mixing the distillation residue with normal incinerable waste in the approximate ratio of 1:10, will not significantly increase the halogen content of the waste and will, therefore, not affect the corrosion rate of incinerator components. Incineration therefore is a viable option for the disposal of Freon waste. The distillation unit recommended should operate in this range to ensure its effectiveness for all the waste streams expected to be generated. To minimize handling of the waste residue following distillation, the distillation unit waste compartment should be equipped with an incinerable liner.

job	file	date	report no.
740632-259-562	837.83	December 12, 1985	85-330-K

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To: Mr. G.H. Williams
Manager
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DISTILLATION OF LIQUID WASTE FROM THE FREON-BASED DRY CLEANING PROCESS

J.P. Krasznai and R.K. Cleary

The solidification of liquid waste from the Freon-based dry cleaning facility at BNPD would result in an increase in waste volume. A more desirable option is to incinerate the waste. This is a viable option provided the Freon content of the waste is reduced to the point where corrosion of incinerator components by acid gases is not a concern.

Distillation in the range 60 - 85°C has been shown to reduce the Freon content of all waste samples to <4%. The distillation unit should be operable in this range and be equipped with an incinerable waste container liner for ease of handling of the residue.

INTRODUCTION

The Bruce Nuclear Power Development (BNPD) Services Department uses Freon 113 as the solvent in its dry cleaning laundries. There are four Health Physics machines and two Marvel machines. The liquid waste arising from the machines is slightly radioactive and its storage presents a problem because the Waste Operation Site licence does not permit the storage of radioactive liquids. A previous report/1/ recommended absorption of the waste onto a solid matrix to avoid dispersion if the waste container was breached. This technique, however, results in an increase in the waste volume. Incineration, a more preferred option, was not recommended unless the Freon content of the samples could be substantially reduced thereby minimizing the production of corrosive gases during incineration. The work presented in this report deals with efforts to reduce the Freon content of the samples by simple distillation.

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DISCUSSION

(a) Distillation

One sample from each of the six machines was received (Table 1) and the Freon content determined by gas chromatography (Table 2). Three samples had appreciable quantities of Freon with one sample from the Health Physics machine, CM4, containing 90% Freon in the waste stream. This large variability in the Health Physics Machine samples indicates that the Freon content in the waste is more a function of the way each machine is operated than the type of machine.

Approximately 200 mL of each sample was heated for two hours at 60°C to determine how much Freon could be distilled from the samples. As Table 2 shows, greater than 90% of the Freon could be removed under these conditions from two of three high Freon samples (CM4 and CM12). The third sample CM5 required two hours at 80°C to reduce the Freon content from 16.3% to 3.8%. The physical appearance of samples CM5 and CM12, which have nominally the same Freon content, are very different, suggesting that in CM12, where there are two distinct phases, the Freon is essentially a separate phase, which explains the ease with which it is distilled. Sample CM5 on the other hand contains primarily one liquid phase which is quite viscous and oily in appearance. In this sample the Freon is likely a volatile solute in a predominantly organic solvent and hence the boiling point of the Freon will be higher than that of the pure material.

The last column of Table 2 shows the total halogen content of the waste after distillation at 60°C for two hours. The data includes sources of chlorine other than Freon. This was calculated by measuring the total elemental chlorine in the sample using neutron activation analysis/2/ and adding to this value the total elemental fluorine content of the sample calculated from the GC data assuming no other source of fluorine than Freon 113. The total halogen content of the waste allows a comparison with the halogen content of normal reactor operating waste which is routinely incinerated. A program is underway to obtain this information/3/. Some preliminary information based on approximately 700 bags of incinerable waste suggests that the halogen content of the waste is in the range of 2 - 7% by weight. The high value is based on the examination of some Pickering NGS Unit 1/2 waste where the proportion of PVC plastic was much higher than in normal reactor operating waste. Comparison of this with the halogen content of Freon waste after distillation (Table 2) indicates that by judicious dilution of the Freon waste with normal incinerable waste (approximately 1:10) the halogen content of the mixture can be kept to levels within the range of the halogen content in normal incinerable waste. Incineration of

TABLE 1

FREON DRY CLEANING WASTE PHYSICAL DESCRIPTION

Sample	Origin	Appearance (before distillation)	Density (g/mL)	Appearance (after distillation)
CM3	Health Physics	One liquid phase, light brown thin liquid	1.02	No change
CM4	Health Physics	One liquid phase, dark brown thin liquid	1.48	No change
CM5	Health Physics	One liquid phase, dark brown viscous liquid viscous sludge on bottom	1.06	No change
CM6	Health Physics	White liquid brown sludge containing particulate on bottom	1.00	No change
CM12	Marvel	Two liquid phases present clear liquid on top dark brown liquid on bottom	1.10	No change but volume ratio of bottom phase to top phase is less
CM13	Marvel	One liquid phase dark brown viscous liquid with sludge on bottom	0.98	No change

TABLE 2

Sample	Freon Content (g/kg)			Total Halogen Content (g/kg)
	Before Distillation	After (60°C)	After (80°C)	After Distillation at 60°
CM3	0	0	-	2
CM4	897	50	-	225
CM5	163	155	38	138
CM6	7	3.5	-	92
CM12	170	1	-	15
CM13	7	3.2	-	30

the residue following distillation is a viable option for managing this type of waste. In fact, although somewhat unconventional, the practice at the Ginna Nuclear Plant in Rochester, is to drum Freon waste and leave the drums open so that the excess Freon can evaporate. Subsequently, the residue is incinerated at a local hospital incinerator.

(b) Waste Residue Handling

The residue after removal of the Freon 113 is a mixture of water, oil/grease and particulate. Since detergent is also added to the Freon 113, the organic material can be in a form of an emulsion as well as a sludge. In view of the low activity levels in the waste (0.1 uCi/L) the handling of the residue will not be of concern from a radiological safety standpoint. Nevertheless, it is desirable to minimize handling of the residue before incineration. Two possible methods are available for introducing the Freon waste residue into the incinerator:

(a) Pump it in as a liquid via the waste oil addition system:

(b) Manually load the material the same way as normal incinerable waste.

A number of problems are associated with (a). Firstly, it requires another waste handling step to load the waste into the waste oil tank. Secondly, the Freon waste contains a significant amount of sludge which would not only build up at the bottom of the tank but could block the injection lines to the incinerator which are only 3/8" diameter.

The manual loading option would require that the waste be contained in relatively small (10 - 15L) incinerable containers to facilitate loading. To minimize waste handling, the suggestion by RMEP/4/ that the distillation unit be equipped with removable, incinerable waste container(s) such that the waste can be transferred from the distillation unit to the incinerator directly has a lot of merit. Without such containers, the waste residue would be difficult to remove. Furthermore, over a period of time, the residue would build up in the distillation unit, the consequences of which, will be to slowly reduce the efficiency of the unit because the residue will act as a solvent for the fresh Freon waste, thereby raising its boiling point. In addition, in view of the large variability in the composition of the waste with respect to water, organic liquid content (including Freon 113), the distillation unit must be able to operate in the 60 - 85°C temperature range. Operation at the high end will result in

water coming off with the Freon but this is not considered to be a problem because (a) the water is immiscible with Freon 113 and can be easily skimmed off the top and (b) water is routinely added to Freon 113 at the start of the dry cleaning cycle and so its removal may be redundant.

CONCLUSIONS

1. The waste stream from the dry cleaning machines is highly variable with Freon content ranging from 1 - 90% by weight. The Freon content seems to be more a function of the cleaning operation (items to be cleaned; cleaning cycle duration) than the machine design.

2. Incineration is a viable option for disposing of the waste provided the Freon content is first reduced by distillation. By judicious mixing of Freon waste with routine incinerable waste (1:10), the halogen content of the mixture will not be increased significantly to cause an increase in the corrosion of incinerator components.

3. The distillation unit should operate in the range 60 - 85°C and the waste container should be equipped with removable incinerable liner(s).

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